PATENT SPECIFICATION

NO DRAWINGS

916,075

Date of Application and filing Complete Specification Dec. 23, 1959.

No. 43708/59.

Application made in United States of America (No. 846236) on Oct. 14, 1959.

Complete Specification Published Jan. 16, 1963.

Index at acceptance: —**Classes 87(2), A1R(14C1X:54:86); and 2(6), P8D(2B2:5), P8K(4:8), P8P(1E1: 4C:5).**

International Classification: —**B29d, f. C08f.**

COMPLETE SPECIFICATION

Method of Moulding Composite Polymerized Articles

We, H. D. JUSTI & SON, INC., of 32nd & Spring Garden Streets, Philadelphia 4, State of Pennsylvania, United States of America, a corporation organised under the laws of the State of Pennsylvania, one of the United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to a method of manufacturing composite moulded polymerized articles of acrylic resin, the articles being useful in the form of artificial teeth and dentures, plastic inlays, plastic jewelry, etc., and is based upon the discovery of a novel bonding procedure which takes place between contacting surfaces of a preformed polymerized methacrylate ester element and a preformed unpolymerized methacrylate ester element joined by moulding, if during the preforming and curing of said polymerized methacrylate ester element a specific type of removable sheet liner material is interposed between the bonding surface of said element and the metal surface of the mould which is used for preforming said element, whereby the interposition of said liner material develops a chemically reactive surface for bonding to the unpolymerized methacrylate ester element.

The removable sheet liner material which is used during curing of the polymerized methacrylate ester element creates a chemically reactive bonding surface of the preformed polymerized methacrylate ester element which is believed to be due to a condition of incomplete polymerization which is confined to a very thin layer at the surface of the polymerized preform between the liner and the interior body portion of the preform. Improved chemical bonding takes place between the unpolymerized methacrylate ester element and the polymerized methacrylate ester element when there is present in the polymerized element, when it is formed and cured, a polyfunctional polymerizable cross-linking monomer such as polyethylene glycol dimethacrylate or allyl methacrylate.

The unpolymerized methacrylate ester element which is provided for composite bonding and moulding operations in accordance with the invention is prepared by mixing a slurry of finely divided polymerized methacrylate in liquid methyl methacrylate to which is added a free radical polymerization catalyst such as benzoyl peroxide, lauroyl peroxide, methyl ethyl ketone peroxide, or cumene hydro peroxide, these being usable with promoters such as cobalt naphthenate and tertiary amines. With benzoyl or lauroyl peroxide there may be used tertiary amine promoters such as dimethyl para toluidine, benzene sulfinic acid or toluene sulfinic acid.

It is not unlikely that the incompletely polymerized methyl methacrylate and the cross-linking agent which are present at the liner treated surface and which are confined to a thin layer at the surface undergo further polymerization during the subsequent moulding and joining operation to bond to the unpolymerized methacrylate ester element in order to form a composite moulded structure.

It is well known that the addition of polyfunctional monomers to polymerizable methacrylate ester compositions provides harder, more heat resistant and more scratch resistant polymerized methacrylate ester products with improved impact resistance. See pages 208—210, "Vinyl and Related Polymers", C. E. Schildknecht, 1952, John Wiley and Sons Inc.

If this known hardening procedure of adding a cross-linking agent for fabrication of the polymerized preform is followed and if the interposition of the special sheet liner

for creating a potentially adhesive surface on the preform during moulding is omitted, the resulting polymerized preform exhibits no chemical bonding to an unpolymerized methacrylate ester element. Unless the surface of the cross-linked polymerized preform is roughened mechanical bonding is also very poor.

Accordingly, the interposition of the liner sheet to create a latent adhesive surface, i.e. a potentially adhesive surface, the polymerized preform is an essential feature of the invention in order to achieve superior bonding to the unpolymerized methacrylate ester element in accordance with the invention.

In accordance with the invention there is added to the latent adhesive preform composition from 2 to 20% by weight of a polyfunctional methacrylate monomer as cross-linking agent such as allyl methacrylate, methallyl methacrylate, ethylene dimethacrylate or polyethylene glycol dimethacrylates including diethylene glycol dimethacrylate, triethylene glycol dimethacrylate or tetraethylene glycol dimethacrylate.

During the subsequent joining of the latent adhesive polymerized preform to the unpolymerized preform by moulding, the polyfunctional monomer apparently diffuses from the surface of the latent adhesive preform into the body portion of the unpolymerized preform. It has been observed that the composite products made by moulding and incorporating cross-linking agents in a latent adhesive preform bonded to an unpolymerized preform display outstanding adhesion characteristics at the interface between the latent preform and the unpolymerized preform after moulding.

The production and use of peroxide catalyzed methacrylate monomer-polymer doughs containing from 25—40% liquid monomer and 60—75% of very finely divided polymer powder for moulding small dental parts and composite teeth from preform parts is well known.

The preforms used for the production of composite teeth from such doughs have previously been assembled and moulded at temperatures of about 175° F. to 300° F. and at pressures of 50 psi up to 200 psi.

However, in the practice of the present invention it is preferred to form the latent adhesive preform from such a dough containing a cross-linking agent in a first stage under a higher pressure, e.g., from 100 psi to 2000 psi, preferably from 800—2000 psi to form an initially shaped mass, said latent adhesive preform being cured in the mould with the liner interposed between the latent adhesive surface and the mould surface at a polymerizing temperature of about 180° F.—210° F. and under a curing pressure of about 800—5000 psi for about from 1½—10 minutes. The latent adhesive preform so treated with the liner is thus put into condition for joining to an unpolymerized preform after the first stage curing.

The unpolymerized preform is formed in similar manner but the step of applying the liner to create the latent adhesive surface of the first preform is omitted. The preform is formed at room temperature under a pressure of 100—2000 psi but no curing takes place.

After the latent adhesive preform is subjected to first stage curing with the liner interposed between the surface which is to be rendered latently adhesive and the surface of the mould, the latent adhesive preform is juxta-posed with an unpolymerized preform and the second stage curing is carried out at a temperature of 250—350° F. and under a pressure of 1500 psi to 5000 psi for from 1½ to 10 minutes to thereby produce the composite tooth structure.

It is an essential requirement of this invention that the liner sheet which is interposed between the methacrylate ester monomer-polymer dough and the metal wall of the mould cavity in order to develop the latent adhesive surface characteristics of the latent adhesive rigid preform be non-adherent to the monomer-polymer composition during the first curing operation at elevated temperatures and pressures, i.e. from 180—210° F. and 800—5000 psi for from 1½ to 10 minutes.

It has been found that the selection of any heat-resistant material for the liner is not, of itsself, sufficient to create the latent adhesive surface characteristics at the liner treated surface of the latent adhesive preform. Only certain heat-resistant liner materials are successful. Heat resistant gum rubber and heat-resistant polyethylene terephthalate (Mylar) films, in thickness up to 10 mils were found to be non-adherent to methyl methacrylate monomer-polymer doughs at room temperature but became adherent during curing the above-stated conditions in the mould so that the latent adhesive surface for chemical bonding was not obtained. Similarly heat-resistant polyvinylidene chloride liners (Saran) were unsatisfactory due to adhering to the cured preform thereby preventing the achievement of a patent adhesive surface on the rigid preform for chemical bonding. Dry heat-resistant Cellophane was found to be unsatisfactory, due to adhesion to the surface of the rigid preform after first stage curing. The dry Cellophane was also found to be embrittled. Highly plasticized Cellophane (excess of glycol or glycerol plasticizer) which was wet with the plasticizer did not adhere to the preform during curing but also did not develop the latent adhesive surface on the rigid preform. The words "Mylar", "Saran" and "Cellophane" are Registered Trade Marks.

Accordingly, it was surprising to find that four materials for the liner were successful

in achieving the necessary latent adhesive characteristic of the surface of the preform for chemical bonding in the subsequent laminating operation by moulding. The materials successfully employed are the following:—

1. High temperature resistant linear polyethylene having a molecular weight of about 50000 or higher, a density of 0.93—0.95 g./c.c., heat resistance up to 250° F., a melting point of about 130° C. or higher, exemplified by Hi-fax sheet (E. I. duPont and Co.), Marlex (Registered Trade Mark) sheet (Phillips Petroleum Company), and Grex sheet (W. R. Grace & Co.).

2. Polytetrafluoroethylene.

3. High temperature resistant polyvinyl alcohol.

4. 6,6 nylon of melting point about 265° C. and density in crystalline form of 1.14 grams per cubic centimetre, this nylon being the condensation product of hexamethylene diamine and adipic acid.

These heat-resistant materials in the form of sheets of from 1—10 mils in thickness are effective as liner sheets for developing a latent adhesive chemical bonding surface on the acrylic rigid preform which has been subjected to the first curing step in the mould at a temperature of about 180—210° F. and under a pressure of 800—5000 psi for from 1½—10 minutes.

Accordingly, an object of the invention is to prepare a latent adhesive surface on a rigid acrylic resin part formed in a metal mould by polymerizing an acrylic monomerpolymer dough by interposing a removable heat-resistant liner sheet, made of a material as specified in the preceding paragraph but one, between the surface of the acrylic part being moulded and the metal wall of the mould whereby the surface of the acrylic part is modified even though the polymerization in the mould has resulted in the production of a completely rigid acrylic resin formed product, this product being thereby rendered suitable for chemical bonding to a rigid unpolymerized acrylic product, the chemical bonding taking place in a mold by juxtaposing both products under curing heat and pressure.

A further object of the invention is to prepare a highly effective latent adhesive surface on a rigid acrylic resin part formed in a metal mould by interposing a heat-resistant liner sheet, as specified in the preceding paragraph but two, in which a cross-linking agent for the acrylic monomer-polymer dough composition is incorporated in said dough composition in an amount of from 2 to 20% by weight of said dough composition and bonding is subsequently effected, *in situ*, to an unpolymerized acrylic part during a subsequent moulding and laminating operation carried out at an elevated temperature and pressure.

Other and further objects will become apparent from the following detailed description and examples of several typical forms of the invention, it being understood that this description is by way of illustration only and that modifications may be carried out as will appear to those skilled in the art which fall within the scope of the invention.

In carrying out the invention in an illustrative form, a first mixture of a selected monomer, methyl methacrylate plus a small percentage of ethylene glycol dimethacrylate, and a selected polymer, polymethyl methacrylate, is made in a mass of dough-like consistency, which, when polymerized, has a predetermined shape, illustratively, in the case of a tooth, the gingival or lingual part of a composite tooth.

A brief comparison which illustrates the difference in bonding achieved in commercial procedures and the procedure of the invention is set forth below.

A first cross-linked and pigmented polymerized part was prepared by moulding an intimate mixture of a methyl methacrylate monomer-polymer dough containing 2.4 parts of finely divided solid methyl methacrylate polymer (6% through 60 on 100 mesh, 40% through 100 mesh on 150 mesh, about 34% through 150 mesh on 250 mesh, about 20% through 250 mesh, Tyler Standard Sieve), 1 part of methyl methacrylate monomer, 0.02 part of benzoyl peroxide and 0.30 part of ethylene glycol dimethacrylate as cross-linking agent under a pressure of 2000—2500 psi. at a temperature of 205° F. for about 3—5 minutes. A standard amount (5%) of white titanium dioxide pigment was added to the dough. The form of the mould part was that used for making a composite incisor tooth. The first mould part had a highly glossy surface exterior.

To the first moulded tooth part there was applied an overlay of the same dough composition as defined in the previous paragraph but which was tinted with iron oxide to provide a different visual appearance to the overlay. The overlay was bonded by moulding to the first mould part at a temperature of 250° F. and pressure of 2000 psi for a period of three minutes.

This composite tooth was picked apart by prying with a sharp-pointed pick. After carefully picking off the polymerized dough overlay, the surface of the first rigid body part which was brought by a moulding into contact with the second part formed by the dough overlay was completely exposed. This first part surface was slightly less glossy than before juxtaposition with the dough overlay. The polymerized dough overlay was successfully pried off as an intact piece. Accordingly, it was concluded that the bonding achieved

was weak and mainly mechanical bonding.

The incisal of the above mentioned tooth was ground from the lingual (back) surface on a grinding wheel. The hardened labial portion chipped away on the wheel exposing the rigid first part member, this also demonstrating the weakness of mechanical bonding.

In contrast a tooth made in accordance with the procedure of Example I of the invention (except that the same composition as above was used) and using the liner sheet material to develop a latent adhesive surface on the first moulded part, i.e. the latent adhesive preform, resulted in a composite tooth which could not be pried apart with the pick to expose the surface of the rigid moulded part and which when ground at the incisal in the same manner as the first tooth tested permitted an even wearing away of both front and back parts without any fracture of either part or any separation at the bondo. Fracpart or any separation at the bond. Fracplace either below the contacting surface of front and back portions or above the contacting surface. In no instance was a substantial bond interfacial area exposed. It appeared that a depth of bond at the interface in both directions, front and back, was achieved, thus indicating that the bond is entirely different in character from the mechanical bonding achieved in the absence of use of the present liner material.

In another embodiment of the invention the first latent adhesive preform which contains as a component of its dough composition a cross-linking agent such as ethylene glycol dimethacrylate may be faced with a thin preformed layer of methyl methacrylate dough composition, e.g., a dough mixture of polymethyl methacrylate powder and methyl methacrylate liquid before joining to the second unpolymerized mass in forming the composite tooth under heat and pressure. The interposition of a thin joining layer of the aforesaid dough composition between the preform and the second unpolymerized dough mass appears to enhance the tenacity of the bond and it appears that the cross-linking agent can diffuse through this thin interposed layer. It is significant that enhanced bonding is achieved in such a short curing cycle as shown in the present examples whereas prior procedures require much longer curing time in the mould.

In comparison with teeth hitherto made commercially from unpolymerized preforms which are bonded *in situ* by moulding, the composite teeth made in accordance with the present invention can be made in greater dimensional accuracy for each of the parts brought together and bonded in the mould. The dough preform parts used in the known process tend to run or distort slightly during *in situ* moulding. Precise duplication of these differently shaded parts is not achieved due to this distortion. With the insistence upon more exacting specifications for precise duplication of shading as it appears in natural teeth, this being different at the incisal tip and the lingual, mesial and distal surfaces of the teeth, there has arisen a need to improve the accuracy of manufacturing to improve the quality and appearance of the teeth made by the known process. This need is satisfied by the present invention.

A further disadvantage of the teeth made by the known process is the tendency to porosity which occurs by reason of minute displacement of the tapered dough sections during *in situ* moulding. This porosity provides a site for water absorption. The lower porosity achieved in accordance with the present invention by the forming of a rigid latent adhesive preform results in teeth not subject to this water sorption. Also the lower porosity of teeth made by the present invention provides composite acrylic teeth of greater density which have better wearing qualities.

The invention is further illustrated in the examples which follow:—

EXAMPLE I.

METHOD OF MOULDING COMPOSITE POLYMERIZED TEETH.

The following example describes the manufacture of plastic teeth utilizing a three piece mould as disclosed in U.S. Patent Specification No. 2,409,783. One part of this mould is used to preform and cure a particular shaped portion of the tooth and additional plastic material is added in the final moulding step to obtain a controlled blending of two different shades.

The materials used are dough mixtures of liquid methyl methacrylate monomer and a suitable cross-linking monomer mixed with a finely divided methyl methacrylate polymer to form a handleable dough capable of being moulded by standard compression moulding techniques.

MIXING OF DOUGH.

The above-mentioned methyl methacrylate polymer is mixed with a polymerizable liquid methyl methacrylate monomer in a ratio of from 1.8 to 2.6 parts by weight of polymer to 1 part by weight of the monomer and as cross-linking agent, 5% by weight of the composition of ethylene glycol dimethacrylate. The mixture is allowed to stand for from 5 to 35 minutes after which period of time a handleable dough is formed.

DOUGH PREFORM.

LINGUAL PREFORM.

The above formed dough is pressed between two polyethylene sheets in a mould to form a doughnut shaped preform under pressure of about 800 psi—1000 psi. The pre-

form may be moulded under a pressure of from 100 psi to 2000 psi if desired.

LABIAL PREFORM.

A dough of the same composition as described above, is pigmented to a different shade and is placed between two polyethylene sheets and pressed in a mould under a pressure of 800 psi—100 psi to form a thin, flat disc having a rectangular cross section. The preform is moulded at 100—2000 psi.

DOUGH PREFORM DRYING.

To assist in the removal of excess monomer a drying operation may be performed as follows:—

The doughnut shaped lingual preform is laid out and one of the polyethylene sheets (see description of first stage curing) is removed and the dough allowed to air dry for a period of from 3 to 5 minutes. This step aids in the elimination of porosity from the final moulded article.

The dried side of the doughnut shaped dough preform is placed toward the labial or buccal side of the mould and the undried side is placed toward the lingual or back side of the mould having removed the polyethylene sheet from the undried side and having placed it on the dried side of the doughnut shaped preform. The top half of the mould is put into place and closed under a pressure of from 500 to 2500 psi; the preferred pressure being 1500—1800 psi.

The polyethylene sheet has been left in place on the labial or buccal surface to act as a temporary liner so the tooth shaped dough preform will remain in the lingual or back half of the mould when the mould is opened. In both cases, the mould is opened and the polyethylene sheet removed from the labial or buccal side.

The back or lingual portion of the mould containing the tooth shaped dough preform is placed in a drying oven at a temperature of from 25 to 75° C., the preferred temperature range being 60—65° C. These tooth shaped dough preforms are allowed to remain in the drying oven from 1 to 10 minutes. This drying procedure insures the removal of the volatile methacrylate ester monomer from the surface and decreases the amount of porosity in the final moulded piece.

FIRST STAGE CURING.

The back or lingual portion of the mould containing the tooth shaped dough preform is removed from the drying oven. A polyethylene liner sheet of the temperature resistant high density type, i.e., Hi-fax, Marlex-50, or Grex, is placed in contact with the exposed dried, labial surface of the preformed dough shape and the component (labial or buccal forming) top of the mould is placed over this polyethylene liner sheet. The mould is closed. The tooth shaped preform faced with the temperature resistant polyethylene sheet in the closed mould is then polymerized at a temperature of from 180 to 210° F., a pressure of 800 psi to 5000 psi for from 1½ to 10 minutes, the preferred temperature range is 190—205° F. at a pressure of 2000 psi to 2500 psi for about 3—5 minutes.

Without the use of the temperature resistant polyethylene liner sheet during the first stage curing, a satisfactory bonding of the labial portion to the lingual portion as described later in this example is not accomplished.

SECOND STAGE CURING.

The mould now contains the polymerized preform. The mould is removed from the open press without cooling. The labial or buccal forming top is removed. The temperature resistant polyethylene liner sheet is also removed. Both of the polyethylene sheets used to form the labial preform disc are removed. The labial dough preform is not subjected to any drying operation and is put into place against the surface of the previously polymerized lingual portion. This portion was in contact with the temperature resistant polyethylene liner sheet during the first stage curing operation. The mould top is then put into place with the labial dough preform directly in contact with the metal mould surface.

The mould is closed and placed under a pressure of from 50 p.s.i. to 1000 p.s.i. and then placed in a press operating at a temperature of from 250° to 350° F. and a pressure of from 1500 p.s.i. to 5000 p.s.i. for from 1½ to 5 minutes.

COOLING.

Without opening the mould it is transferred to a press operating at room temperature and the pressure is dropped to about 600—1000 p.s.i. After a period of time sufficient to cool the mould to less than 100° F., e.g., about 2—3 minutes, the mould is opened. In this example it is seen that the temperature in the second stage of curing is higher than in the first stage of curing.

EXAMPLE II.

In this example, the proceedings as outlined in Example I are followed except that the labial or incisal portion is cured first with a liner sheet in place, then a doughnut shaped dough comprising the lingual or body portion is put into place and the two (rigid labial, dough lingual) are polymerized to adhere together.

EXAMPLE III.

The following example describes the manufacture of plastic teeth utilizing a three piece mould as in Example I.

MIXING OF DOUGH.

1. LINGUAL OR BODY DOUGH.

Polymethyl methacrylate is mixed with methyl methacrylate monomer containing ethylene glycol dimethacrylate in a ratio of 1.8 to 2.6 parts by weight of polymer to one part by weight of monomer and allowed to stand for from 5 to 35 minutes after which period of time a handleable dough is formed.

2. INTERMEDIATE DOUGH.

Polymethyl methacrylate is mixed with methyl methacrylate monomer in a ratio of 1.8 to 2.6 parts by weight of polymer to one part by weight of the monomer and allowed to stand for from 5 to 35 minutes after which period of time a handleable dough is formed.

3. LABIAL OR TIP DOUGH.

Polymethyl methacrylate is mixed with methyl methacrylate monomer containing ethylene glycol dimethacrylate in a ratio of 1.8 to 2.6 parts by weight of polymer to 1 part by weight of the monomer and allowed to stand for from 5 to 35 minutes after which period of time a handleable dough is formed.

DOUGH PREFORMS.

1. LINGUAL OR BODY PREFORM.

The above formed dough is pressed between two polyethylene sheets in a mould under 800 p.s.i. to form a doughnut shaped preform. The preform may be moulded at from 100 p.s.i. to 2000 p.s.i. if desired.

2. INTERMEDIATE PREFORM.

The above formed dough being pigmented to the same shade as the body dough is placed between two polyethylene sheets and placed in a mould under 800 p.s.i. to form a flat disc having a rectangular cross section of uniform thickness 0.010 inch thick. The preform may be moulded at from 100 p.s.i. to 2000 p.s.i. if desired.

3. LABIAL PREFORM.

The above formed dough being pigmented to a different shade is placed between two polyethylene sheets and pressed in a mould under 800 p.s.i. to form a thin flat disc having a rectangular cross section. The preform may be moulded at from 100 p.s.i. to 2000 p.s.i. if desired.

TOOTH SHAPED DOUGH PREFORM.

In order to assist in the removal of excess monomer certain drying operations are performed on the doughnut shaped lingual preform as well as on the intermediate preform.

The doughnut shaped preform is placed in the lingual part of the mould and covered with a polyethylene sheet. The top half of the mould is put in place and the mould closed under 1700 p.s.i. The mould is opened and the polyethylene sheet removed. One side of the intermediate preform having been exposed by the removal of the polyethylene sheet is placed so that the unexposed side is in contact with the exposed portion of the tooth shaped dough preform. The polyethylene sheet having been removed and placed on the exposed side and again the top half of the mould is put in place and the mould closed under 1700 psi. Due to the differential drying of the doughnut shaped body preform and the intermediate preform the intermediate dough displaces a portion of the body dough. The intermediate preform, at a thickness of from 0.005 to 0.015 inch allows a non-crosslinked surface to be available for bonding to the labial preform material in the final moulding operation.

FIRST STAGE CURING.

The top half of the mould is removed, the polyethylene liner sheet removed and replaced with a polyethylene liner sheet of the temperature resistant high density type, and the top half of the mould is replaced. The closed mould now contains the tooth shaped preform which consists of a crosslinked layer laminated to a non-crosslinked layer. The laminated preform is polymerized at a temperature of from 180 to 210° F. and a pressure of 2500 psi for from 1½ to 10 minutes. The non-crosslinked layer serves as an intermediate layer in the second stage curing operation, below.

The labial surface of this intermediate layer remains non-crosslinked during the first stage curing and provides a surface which can be attacked by the free monomer available in the labial dough preform, thereby giving rise to a chemical bonding of these two surfaces. During the second stage curing operation there is sufficient migration of the crosslinking agent from the labial dough into the non-closslinked layer to provide sufficient crosslinking so that the entire finished moulded tooth is crosslinked. The finished tooth has superior properties specifically with regard to attack by solvents which, were the material non-crosslinked, would cause objectionable crazing.

SECOND STAGE CURING.

The mould containing the polymerized laminated preform is removed from the press and is opened without cooling. The top half of the mould is removed and the previously mentioned labial dough preform, without being subjected to any drying operation is separated from both of the polyethylene sheets and is put into place against the non-crosslinked surface of the polymerized lingual portion. The mould top is then put into place with the labial dough preform encased between the top and the polymerized laminated preform. The mould is closed under a pressure of 100 p.s.i. and placed in a press

operating at a temperature of from 250 to 350° F. and a pressure of 2500 p.s.i. for $1\frac{1}{2}$ to 10 minutes.

COOLING.

Without opening the mould it is transferred to a press operating at a temperature of from 45 to 100° F. under a pressure of 800 p.s.i. for a period of time sufficient to bring the mould temperature down to from 80 to 100° F.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

WHAT WE CLAIM IS:—

1. A method of forming a moulded composite article of polymerized methyl methacrylate resin, which method comprises shaping a first dough portion from a dough of mixed finely divided solid polymethyl methacrylate and liquid methyl methacrylate monomer with from 2 to 20% by weight of a polyfunctional polymerizable monomer as cross-linking agent while simultaneously contacting one surface of the first dough portion with a heat-resistant non-adherent liner sheet made of a synthetic resin selected from linear polyethylene, polytetrafluoroethylene, polyvinyl alcohol and heat-resistant nylon, said liner having a thickness of from 1 to 10 mils, polymerizing said first dough portion by moulding said dough faced with said liner sheet at elevated temperature and pressure to provide a latent adhesive preform having substantially the same shape as in the moulded composite article but also having an incompletely polymerized latent adhesive surface portion under said liner sheet, removing said liner sheet, assembling against said latent adhesive surface portion of said preform a second dough portion formed from said dough, said second portion being in an unpolymerized state and moulding said latent adhesive preform and said second dough portion at elevated temperature and pressure to polymerize said second dough portion and said incompletely polymerized surface portion of said preform while bonding the latter with the contacting surface of said second dough portion.

2. A method according to Claim 1, wherein the cross-linking agent is selected from allyl methacrylate, ethylene dimethacrylate and polyethylene glycol dimethacrylate.

3. A method according to Claim 1, wherein a composite tooth is formed by utilizing a plural part separable mould, in one part of which is moulded said first dough portion to form a lingual portion for said tooth and in a second part of which is moulded said second dough portion to form a labial portion for said tooth.

4. A method according to any preceding claim, wherein said first and second dough portions are bonded at a temperature of from 250 to 350° F. and under a pressure of from 1500 to 5000 pounds per square inch for from $1\frac{1}{2}$ to 10 minutes.

5. A method according to any preceding claim, wherein the latent adhesive portion is formed at a temperature of from 180—210° F. and under a pressure of from 800—5000 pounds per square inch for a time of from $1\frac{1}{2}$ to 10 minutes.

6. A method according to any preceding claim, wherein said first portion of dough is dried on one side with the other side faced with said liner for a period of from 3 to 10 minutes at room temperature.

7. A method according to any preceding claim, wherein an intermediate layer of unpolymerized methacrylate ester dough is interposed between said latent adhesive preform and said second dough portion prior to the final bonding and polymerizing step in the mould, thus presenting a non-cross-linked surface available for joining to said second dough portion in the final moulding operation.

8. A method of producing an artificial tooth, substantially as described in any one of the foregoing examples.

9. A moulded composite article of polymerized methyl methacrylate resin, whenever produced by a method claimed in any preceding claim.

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Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1963.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.